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Effect of the Acid Properties on the Diffusion of C_7 Hydrocarbons in UL-ZSM-5 Materials

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1. Introduction

Mesoporous UL-ZSM-5 materials have zeolitic structure in the form of nano-particles inter-grown in the walls of the amorphous wormhole-like aluminosilicate mesoporous precursor, and were shown to exhibit an intermediate acidity between the parent mesoporous precursor and ZSM-5 zeolite [1,2]. These materials combine the advantages of both, i.e., microporous crystalline zeolites (strong acidity and good thermal/hydrothermal stability), and mesoporous materials, e.g., highly ordered large pores and high specific surface areas. They have been considered to have a great potential for applications in catalysis and adsorption technologies, particularly as acid catalysts for bulky hydrocarbons conversion [3].

Recently the transport properties of n-heptane and toluene in UL-ZSM-5 materials with Si/Al ratio of 50 have been thoroughly investigated using the Zero Length Column (ZLC) technique [4]. The transport of n-heptane was found to be mainly controlled by mesopore diffusion in the main channel structure, while that of toluene was dominated by intrawall diffusion process. However, up to now no study related to the influence of acid sites on the transport property of biporous micro- and meso-porous materials has been reported yet. Thus, the main objective of this study is to clarify the influence of acid sites on the diffusion of C_7 hydrocarbons in UL-MFI materials, with different Si/Al ratios, using the ZLC technique.

2. Experimental

UL-MFI (Silicalite and ZSM-5 types) materials were prepared according to the synthesis method described by Trong-On and Kaliaguine [1,2]. The calcined UL-MFI solids were further treated with NaCl or NH_4Cl solution to obtain Na- or H-form materials. A microporous ZSM-5 sample with Si/Al ratio of 50 was also synthesized and used as a reference material. The physico-chemical characterisations were performed using BET, SEM, XRD and AAS methods. The acid properties were examined by FTIR of adsorbed pyridine. Desorption rate measurements of n-heptane and toluene were carried out by the ZLC method employing a GC equipped with FID [5].

3. Results and Discussion

The nitrogen adsorption/desorption isotherms of all UL-MFI samples, SEM analysis as well as XRD patterns all reveal the presence of nanocrystals within the mesopore walls. In addition, Al-MAS-NMR analysis confirmed that Al atoms are incorporated in

the walls (microstructure) of these samples [4]. It was also found from FTIR of adsorbed pyridine experimental results that the density of Brönsted acid sites is higher for UL-ZSM-5 treated with diluted aqueous NH_4Cl solution than when treated with diluted aqueous NaCl solution. The number of both Brönsted and Lewis acid sites in Na- and H-form of UL-MFI samples increases with an increase of aluminum content.

Shown in Fig. 1, effective diffusivity values extracted from ZLC desorption results for both sorbates in the UL-MFI samples exhibit a sharp decrease with respect to the increase of micropore volume, which suggests that this trend is attributed to sorbate-acid site interactions. Moreover, activation energy for n-heptane was found to be twice as high as that for toluene. The range of these values is strongly dependent on the Si/Al ratio.

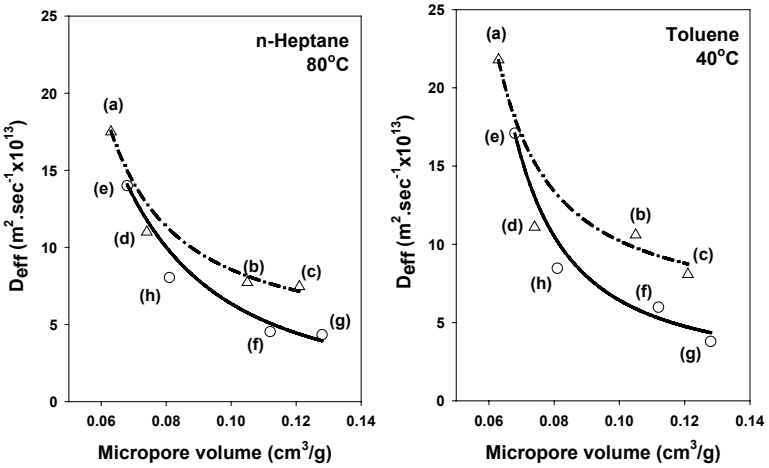

Figure 1. Variation of the effective diffusivity for n-heptane at 80°C and toluene at 40°C with micropore volume in (a) UL-Silicalite-Na^+, (b) UL-ZSM-5-*100*-Na^+, (c) UL-ZSM-5-*50*-Na^+, (d) UL-ZSM-5-*20*-Na^+, (e) UL-Silicalite-NH_4^+, (f) UL-ZSM-5-*100*-NH_4^+, (g) UL-ZSM-5-*50*-NH_4^+ and (h) UL-ZSM-5-*20*-NH_4^+ samples.

Note: Italics in the sample designations denote Si/Al ratios. Solid and dash lines denote the trends for H- and Na-forms, respectively.

The effective diffusivities for both sorbates in UL-MFI materials are much higher than in conventional MFI zeolites. Combined with the higher acidity and higher hydrothermal stability as compared to amorphous mesostructured materials, this suggests that UL-MFI materials could be suitable as catalysts for applications in petroleum refining and fine chemical synthesis.

References

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